

# A Unified Theory of Chemical Reactions

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We propose a new and general formalism for elementary chemical reactions where quantum electronic variables are used as reaction coordinates. This formalism is in principle applicable to all kinds of chemical reactions ionic or covalent. Our theory reveals the existence of an intermediate situation between ionic and covalent which may be almost barrierless and isoenergetic and which should be of high interest for understanding biochemistry.

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Chemical reactions are primarily changes of electronic states (associated with molecular and environmental reorganization) which appears either in radical ionization (redox) or in the forming/breaking of chemical bonds. They can be generally decomposed into sequences of elementary reactions corresponding to single transitions between two different electronic states for example an electron transfer (ET) between a Donor and an Acceptor. The rate of chemical reactions often obeys the Arrhenius law which manifest the existence of an energy barrier between the reactants and the products which has to be overcome by the thermal fluctuations. This energy barrier is usually quite large compared to the ambient temperature energy ( $\approx 0.026\text{eV}$  at  $300\text{K}$ ). There are also chemical reactions which do not obey the Arrhenius law (with a positive energy barrier). This is the situation for *free radicals* with unpaired electrons which are generally highly reactive [2] and generate covalent bonds.

The standard theory for ET (redox) mostly due to Marcus[1], considers the free energy the whole system as a function of the nuclei (reaction) coordinates when the electron is on the Donor site (reactants) or on the Acceptor site (products). These functions are approximate as paraboloids schematically represented fig.1. There are two regimes called normal when at constant coordinates, the electronic excitation from Donor to Acceptor requires to absorb a positive energy  $E_{el}$  and inverted when  $E_{el}$  is negative.

The lowest point at the intersection of these two surfaces determines the minimum free energy  $\Delta G^*$  to be provided to the system for transferring the electron between Donor and Acceptor. This energy barrier may be reached because of the thermal fluctuations of the nuclei with a probability per unit time proportional to  $e^{-\frac{\Delta G^*}{k_B T}}$  which yields the main factor of the Arrhenius law. At this point the two electronic states on Donor and Acceptor are degenerate so that ET may occur by quantum tunnelling. Actually, because of small overlap terms. between the electronic orbitals, degeneracy is raised with a small gap so that the two diabatic surfaces are non intersecting as shown fig.1. Electron hopping from Donor

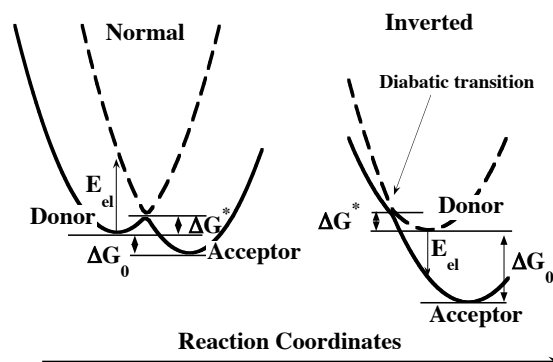


FIG. 1: Standard Theory: The surfaces of energy versus Reaction Coordinates are two intersecting paraboloids, one corresponding to the reactants and one to the products. A small gap opening at intersection determines a lower energy surface and an upper energy surface.

to Acceptor is considered as a probabilistic event which depends on the time during which resonance lasts and thus depends on the phonon frequencies and the temperature. The transition probability between the two diabatic surfaces  $A(T)$  which contributes to the prefactor of the Arrhenius law is empirically calculated from the Landau-Zener model. In the normal regime, ET does not require any diabatic transition while in the inverted regime a diabatic transition from the upper to the lower energy surface is necessary (see fig.1).

A great mystery of the chemistry of life (biochemistry) is that it operates efficiently about room temperature even when involving highly energetic reactions (e.g. oxidation of sugars). Most the released energy remains stored in other chemical forms to be involved later for fueling subsequent bioreactions. Thus, biochemistry essentially operates along nearly isoenergetic chemical paths that is with energy variations and barriers smaller or comparable to the room temperature energy ( $0.026\text{eV}$  at  $300\text{K}$ ). Enzymes generate such chemical paths by triggering specific chemical reactions which could not occur spontaneously. Backward reactions could even be also

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catalysed under changes in the environmental conditions. The unified theory which we outline now, show that such chemical paths may exist by involving both charge and covalent interactions in well-tuned systems (as should be the enzymatic systems).

We start from first principles and consider very generally, the global quantum Hamiltonian  $H$  of our reacting system with interacting electrons  $\alpha$  with coordinates  $\mathbf{r} = \{\mathbf{r}_\alpha\}$  also interacting with a collection of quantum nuclei  $i$  with masses  $M_i$  and coordinates  $\mathbf{R}_i$ . It can be written with the general form  $H = \sum_i \frac{\mathbf{P}_i^2}{2M_i} + H_e(\mathbf{R})$  as the sum of the kinetic energy operator of the nuclei which is a function of the conjugate operators  $\mathbf{P}_i = \frac{\hbar}{i} \nabla_{\mathbf{R}_i}$  of the nuclei coordinates  $\mathbf{R}_i$  and the Hamiltonian  $H_e(\mathbf{R})$  which describes the rest that is the whole system of electrons submitted to a potential generated by the nuclei. The standard Born-Oppenheimer (BO) approximation assumes that the global wavefunction has the form  $\Psi(\mathbf{r}, \mathbf{R}, t) = \Phi(\mathbf{R}, t) \psi_0(\mathbf{r}, \mathbf{R})$  where  $\psi_0(\mathbf{r}, \mathbf{R})$  is the electronic groundstate of Hamiltonian  $H_e(\mathbf{R})$ . Its eigenenergy  $E_0(\mathbf{R})$  becomes the effective potential for the nuclei.

We consider now an elementary chemical reaction corresponding to a transition between two electronic states called Donor (initial) and Acceptor (final) so that the electronic state remains confined in a 2D subspace  $\mathcal{E}(\mathbf{R})$  invariant by  $H_e(\mathbf{R})$  spanned by these two states. All the other electronic eigenstates (far in energy) are discarded. It is convenient to choose a LCAO real and orthogonal base  $\psi_D(\mathbf{r}, \mathbf{R})$  representing for example to the electron on a donor site and  $\psi_A(\mathbf{r}, \mathbf{R})$  this electron on an acceptor site. The global wave function has the form  $\Psi(\mathbf{r}, \mathbf{R}, t) = \Phi_D(\mathbf{R}, t) \psi_D(\mathbf{r}, \mathbf{R}) + \Phi_A(\mathbf{R}, t) \psi_A(\mathbf{r}, \mathbf{R})$ .

Then, integration over the electronic variables  $\mathbf{r}$  yields the nuclei Hamiltonian  $\langle \Psi(\mathbf{r}, \mathbf{R}, t) | H_e(\mathbf{R}) + \sum_i \frac{\mathbf{P}_i^2}{2M_i} | \Psi(\mathbf{r}, \mathbf{R}, t) \rangle_r = \tilde{H}_e + \tilde{K}$  which now operates in the two-components wave function space  $\Phi(\mathbf{R}, t) = \begin{pmatrix} \Phi_D(\mathbf{R}, t) \\ \Phi_A(\mathbf{R}, t) \end{pmatrix}$ .  $\tilde{H}_e$  is a  $2 \times 2$  matrix which has the form  $\tilde{H}_e = \begin{pmatrix} E_D(\mathbf{R}) & \Lambda(\mathbf{R}) \\ \Lambda(\mathbf{R}) & E_A(\mathbf{R}) \end{pmatrix}$  only dependant on  $\mathbf{R}$  while the projected kinetic energy operator  $\tilde{K} = \sum_{i,\alpha} \frac{\mathbf{P}_{i,\alpha}^2}{2M_i}$  can be expressed with the following overlap integrals  $a_{i,\alpha}^{n,m}(\mathbf{R}) = \frac{1}{M_i} \int \psi_n(\mathbf{r}, \mathbf{R}) \frac{\partial \psi_m(\mathbf{r}, \mathbf{R})}{\partial \mathbf{R}_{i,\alpha}} d\mathbf{r}$  for  $n, m = D$  or  $A$ . Orthonormalization implies  $\mathbf{a}^{D,D}(\mathbf{R}) = 0$  and  $\mathbf{a}^{A,A}(\mathbf{R}) = 0$  and  $a_{i,\alpha}^{D,A}(\mathbf{R}) = -a_{i,\alpha}^{A,D}(\mathbf{R}) = \frac{1}{M_i} \int \psi_D(\mathbf{r}, \mathbf{R}) \frac{\partial \psi_A(\mathbf{r}, \mathbf{R})}{\partial \mathbf{R}_{i,\alpha}} d\mathbf{r}$  real. We define vector  $\mathbf{A}(\mathbf{R}) = \{a_{i,\alpha}^{D,A}(\mathbf{R})\} = \{-a_{i,\alpha}^{A,D}(\mathbf{R})\}$ . We also define the matrix elements for  $n, m = D$  or  $A$ ,  $w^{n,m}(\mathbf{R}) = w^{m,n}(\mathbf{R}) = \sum_i \frac{1}{2M_i} \int \nabla_{\mathbf{R}_i} \psi_n(\mathbf{r}, \mathbf{R}) \cdot \nabla_{\mathbf{R}_i} \psi_m(\mathbf{r}, \mathbf{R}) d\mathbf{r}$ . Then, the projected kinetic operator  $\sum_i \frac{\mathbf{P}_i^2}{2M_i}$  becomes the  $2 \times 2$  matrix of operators  $\tilde{K} = \begin{pmatrix} \mathbf{K}_{DD} & \mathbf{K}_{DA} \\ \mathbf{K}_{AD} & \mathbf{K}_{AA} \end{pmatrix}$  where  $\mathbf{K}_{DD} = \sum_i \frac{\mathbf{P}_i^2}{2M_i} + \hbar^2 w^{D,D}(\mathbf{R})$ ,  $\mathbf{K}_{AA} = \sum_i \frac{\mathbf{P}_i^2}{2M_i} + \hbar^2 w^{A,A}(\mathbf{R})$ ,  $\mathbf{K}_{DA} = -\frac{i\hbar}{2} (\mathbf{A} \cdot \mathbf{P} + \mathbf{P} \cdot \mathbf{A}) + \frac{\hbar^2}{2} \nabla \cdot \mathbf{A} + \hbar^2 w^{D,A}(\mathbf{R}) = \mathbf{K}_{AD}^*$ .

It is convenient to use the base of the Pauli matrices  $\sigma^x, \sigma^y, \sigma^z$  which fulfills the standard commutation relations  $[\sigma^x, \sigma^y] = 2i\sigma^z$ ,  $[\sigma^y, \sigma^z] = 2i\sigma^x$ ,  $[\sigma^z, \sigma^x] = 2i\sigma^y$  so that the fully quantum Hamiltonian appears a collection of quantum nuclei coupled to a quantum spin

$$\tilde{H} = \sum_i \frac{\mathbf{P}_i^2}{2M_i} + \mathcal{V}_{ph}(\mathbf{R}) + \tilde{\Lambda}(\mathbf{R})\sigma^x + \Pi(\mathbf{R}, \mathbf{P})\sigma^y + \mathcal{W}(\mathbf{R})\sigma^z \quad (1)$$

where  $\mathcal{V}_{ph}(\mathbf{R}) = \frac{1}{2}(E_D(\mathbf{R}) + E_A(\mathbf{R})) + \frac{\hbar^2}{2}(w^{D,D}(\mathbf{R}) + w^{A,A}(\mathbf{R}))$ ,  $\mathcal{W}(\mathbf{R}) = \frac{1}{2}(E_D(\mathbf{R}) - E_A(\mathbf{R})) + \frac{\hbar^2}{2}(w^{D,D}(\mathbf{R}) - w^{A,A}(\mathbf{R}))$ ,  $\tilde{\Lambda}(\mathbf{R}) = \Lambda(\mathbf{R}) + \frac{\hbar^2}{2} \nabla \cdot \mathbf{A}(\mathbf{R}) + \hbar^2 w^{D,A}(\mathbf{R})$  and  $\Pi(\mathbf{R}, \mathbf{P}) = \frac{\hbar}{2} (\mathbf{A}(\mathbf{R}) \cdot \mathbf{P} + \mathbf{P} \cdot \mathbf{A}(\mathbf{R}))$ .

For going further, it is now convenient to assume that 1) The origin of the nuclei coordinates as well as the origin of the energies are chosen at the minimum of potential  $\mathcal{V}_{ph}(\mathbf{R})$  which is supposed to be quadratic with the elasticity matrix  $\bar{\mathbf{M}}$ :  $\mathcal{V}_{ph}(\mathbf{R}) = \frac{1}{2} \mathbf{R} \cdot \bar{\mathbf{M}} \cdot \mathbf{R}$ . 2) We assume a linear behavior for the spin coefficients of  $\sigma^z$  (charge coupling),  $\mathcal{W}(\mathbf{R}) = \mathcal{W}(\mathbf{0}) + \nabla \cdot \mathcal{W}(\mathbf{0}) \cdot \mathbf{R}$ , of  $\sigma^x$  (covalent coupling)  $\tilde{\Lambda}(\mathbf{R}) = \tilde{\Lambda}(\mathbf{0}) + \nabla \cdot \tilde{\Lambda}(\mathbf{0}) \cdot \mathbf{R}$  and of  $\sigma^y$   $\Pi(\mathbf{R}, \mathbf{P}) = \hbar \mathbf{A}(\mathbf{0}) \cdot \mathbf{P}$  (see. [3]). Considering the overlap integrals  $a_{i,\alpha}^{D,A}(\mathbf{R})$  may be small with the LCAO base,  $\mathbf{A}(\mathbf{0}) = 0$  for simplicity (though it would not be a big deal to conserve the coupling with  $\sigma^y$ ). Then, it is convenient to use the base of normal modes obtained by diagonalization of matrix  $\bar{\mathbf{M}}$ .

Hamiltonian (1) becomes those of a single quantum spin 1/2 submitted to a field  $(\epsilon_x, 0, \epsilon_z)$  and coupled a collection of normal modes  $n$  (harmonic oscillators with unit mass and frequency  $\omega_n$ ) by constants  $k_n^x, 0, k_n^z$ .

$$\tilde{H} = \sum_n \left( \frac{1}{2} (p_n^2 + \omega_n^2 q_n^2) + k_n^x q_n \sigma^x + k_n^z q_n \sigma^z \right) + \epsilon_x \sigma^x + \epsilon_z \sigma^z \quad (2)$$

Finally, we use a mean field approximation where the coupling terms  $q_n \sigma^z$  (and similarly for  $q_n \sigma^x$ ) are replaced by  $q_n \bar{\sigma}^z + \bar{q}_n \sigma^z - \bar{q}_n \bar{\sigma}^z$  then neglecting the fluctuation operators  $(q_n - \bar{q}_n)(\sigma^z - \bar{\sigma}^z)$  [4]. We argue the validity of this approximation because the nuclei displacements generated by the molecular reorganization during ET are generally much larger than their zero point quantum fluctuations (especially in biomolecules). Then, it comes out after some calculations that the equations of the time evolution of the observables  $\{\bar{p}_n, \bar{q}_n\}$  and  $\bar{\sigma}^x, \bar{\sigma}^y, \bar{\sigma}^z$  form a closed set (that is do not involve any other observables) which are identical to the dynamical equations of a classical Hamiltonian (2) where the quantum operators  $\{p_n, q_n\}$  and  $\sigma^x, \sigma^y, \sigma^z$  are just replaced by their real observables  $\{\bar{p}_n, \bar{q}_n\}$  and  $\bar{\sigma}^x, \bar{\sigma}^y, \bar{\sigma}^z$ . It turns out that quantum spin  $\varphi_D(t) | \uparrow \rangle \rightarrow +\varphi_A(t) | \downarrow \rangle$  represented in the eigenbase of  $\sigma^z$  (Donor Acceptor) turns out to be submitted to the time dependant classical field with components  $(\epsilon_x + \sum_n k_n^x \bar{q}_n(t), 0, \epsilon_z + \sum_n k_n^z \bar{q}_n(t))$  while the classical oscillators  $n$  are submitted to external time dependant forces  $f_n(t) = k_n^x \bar{\sigma}^x(t) + k_n^z \bar{\sigma}^z(t)$ .

Actually, the motion  $\bar{q}_n(t)$  of each oscillator may be explicitly calculated as the sum of a function of the external force  $f_n(t)$  and a solution of the free oscillator chosen randomly according to the Boltzman statistics as done in [6, 7] so that the nuclei variables be eliminated from the dynamical equation describing the electron dynamics. The spin (or electronic) dynamics is then described by

$$\begin{aligned}
i\hbar\dot{\varphi}_D &= \frac{\partial H_{eff}}{\partial \varphi_D^*} + \zeta^z(t)\varphi_D + \zeta^x(t)\varphi_A \\
&+ \left( \int_0^t \left( \Gamma_{zz}(t-\tau)\dot{Z}(\tau) + \Gamma_{xz}(t-\tau)\dot{X}(\tau) \right) d\tau \right) \varphi_D \\
&+ \left( \int_0^t \left( \Gamma_{xz}(t-\tau)\dot{Z}(\tau) + \Gamma_{xx}(t-\tau)\dot{X}(\tau) \right) d\tau \right) \varphi_A \\
i\hbar\dot{\varphi}_A &= \frac{\partial H_{eff}}{\partial \varphi_A^*} - \zeta^z(t)\varphi_A + \zeta^x(t)\varphi_D \\
&- \left( \int_0^t \left( \Gamma_{zz}(t-\tau)\dot{Z}(\tau) + \Gamma_{xz}(t-\tau)\dot{X}(\tau) \right) d\tau \right) \varphi_A \\
&+ \left( \int_0^t \left( \Gamma_{xz}(t-\tau)\dot{Z}(\tau) + \Gamma_{xx}(t-\tau)\dot{X}(\tau) \right) d\tau \right) \varphi_D
\end{aligned} \tag{3}$$

where the effective Hamiltonian is

$$\begin{aligned}
H_{eff}(\varphi_D, \varphi_A) &= \epsilon_x X + \epsilon_z Z \\
&- \frac{1}{2}\Gamma_{xx}(0)X^2 - \Gamma_{xz}(0)XZ - \frac{1}{2}\Gamma_{zz}(0)Z^2
\end{aligned} \tag{4}$$

and where  $Z = \bar{\sigma}^z = |\varphi_D|^2 - |\varphi_A|^2$  and  $X = \bar{\sigma}^x = \varphi_D^* \varphi_A + \varphi_D \varphi_A^*$ . The memory functions are defined as  $\Gamma_{xx}(t) = \sum_n \frac{(k_n^x)^2}{\omega_n^2} \cos \omega_n t = \int \tilde{\Gamma}_{xx}(\omega) \cos \omega t d\omega$ ,  $\Gamma_{zz}(t) = \sum_n \frac{(k_n^z)^2}{\omega_n^2} \cos \omega_n t = \int \tilde{\Gamma}_{zz}(\omega) \cos \omega t d\omega$ ,  $\Gamma_{xz}(t) = \sum_n \frac{k_n^z k_n^x}{\omega_n^2} \cos \omega_n t$  and fulfill  $0 \leq \Gamma_{zz}(0)$ ,  $0 \leq \Gamma_{xx}(0)$  and  $\Gamma_{xz}^2(0) \leq \Gamma_{zz}(0)\Gamma_{xx}(0)$ . Assuming a large system with many classical oscillators generates a classical Langevin bath [8]. Thus, these functions may be assumed to be smooth and to vanish at large time. but with Fourier transforms which vanish for  $\omega > \omega_c$  where  $\omega_c$  is the maximum phonon frequency. It can be shown indeed that in the absence of random forces the effective energy  $H_{eff}$  necessarily decay (essentially due to non adiabaticity) [7] but the damping is frequency dependant. Actually when the characteristic frequency of the electronic dynamics goes beyond  $\omega_c$ , the effect of damping disappears. The non adiabatic effects thus disappear so that the system obeys again the BO approximation.

This effective Hamiltonian (4) may be obtained as the energy minimum of the whole system at fixed electronic amplitudes  $\varphi_D, \varphi_A$  and with respect to all the nuclei coordinates. A similar one was introduced phenomenologically in [6] without microscopic justifications but the form which was used, was not correct because we omitted covalent terms and artificially introduced extra nonlinear

capacitive terms. These terms actually do not exist because already taken into account in the coefficients of the linear quantum electronic Hamiltonian  $H_{el}$ . Temperature appears in eqs.(3) through the gaussian random forces with correlations fulfilling the Langevin conditions  $\langle \zeta^z(t)\zeta^z(t+\tau) \rangle_t = k_B T \Gamma_{zz}(\tau)$ ,  $\langle \zeta^x(t)\zeta^x(t+\tau) \rangle_t = k_B T \Gamma_{xx}(\tau)$ ,  $\langle \zeta^x(t)\zeta^z(t+\tau) \rangle_t = k_B T \Gamma_{xz}(\tau)$

Defining new conjugate variables  $I_D, \theta_D, I_A, \theta_A$  by  $\varphi_D = \sqrt{I_D} e^{-i\theta_D}$  and  $\varphi_A = \sqrt{I_A} e^{-i\theta_A}$ , and next the conjugate variables  $I = (I_A - I_D)/2 = -Z/2$  and  $\theta = \theta_A - \theta_D$ , this effective Hamiltonian becomes only a function  $-\frac{1}{2} \leq I \leq \frac{1}{2}, \theta \bmod 2\pi$  on a sphere with poles  $I = \pm \frac{1}{2}$  and where  $\theta$  corresponds to the longitude and  $\phi$  defined as  $\sin \phi = 2 * I$  to the latitude. Then  $H_{eff} = -2\epsilon_z I + \epsilon_x \sqrt{1-4I^2} \cos \theta - 2\Gamma_{zz}(0)I^2 + 2\Gamma_{xz}(0)I\sqrt{1-4I^2} \cos \theta - \frac{1}{2}\Gamma_{xx}(0)(1-4I^2) \cos^2 \theta$  represents the true energy surface for ET. At zero temperature (0K) and assuming the damping terms vanishes, the dynamical equations would be those of an integrable Hamiltonian system on a sphere. All trajectories would be periodic on closed orbits defined by a constant energy  $H_{eff}(I, \theta)$ . Figs.2 and 3 show both 3D and contour plots for several examples.

We assume that the (initial) transfer integral  $\epsilon_x$  is small as in the standard theory and that our system is initially at the Donor pole  $I = -1/2$ . The Acceptor pole corresponds to  $I = +1/2$ . When there are no covalent interactions ( $\Gamma_{xx}(0) = \Gamma_{xz}(0) = 0$ ), our theory is nothing but a different representation of the standard Marcus theory except that we now have explicit dynamical equations which intrinsically describe the diabatic transitions through the damping terms. without needing the Landau-Zeener model. The two Marcus energy surfaces are the paraboloids obtained from Hamiltonian (2) where  $\sigma^x = 0, p_n = 0$  and  $\sigma^z = +1$  (electron on Donor) or  $\sigma^z = -1$  (electron on Acceptor) Then the reaction energy is  $\Delta G_0 = 2\epsilon_z$  assumed to be positive, the barrier energy  $\Delta G^* = \frac{(\epsilon_z - \Gamma_{zz}(0))^2}{2\Gamma_{zz}(0)}$  and the electronic excitation energy  $E_{el} = 2(\Gamma_{zz}(0) - \epsilon_z)$ .

In the normal regime, when  $E_{el} > 0$ , the energy surface (see fig.2 left) exhibits a saddle point between donor and acceptor which corresponds to the barrier between the donor and acceptor state. At the inversion point where  $E_{el} = 0$ , the saddle point and the two maxima on the sphere of  $H_{eff}(I, \theta)$  merge with the minimum near the pole  $I = -1/2$  which thus become a single maximum so that in the inverted regime  $E_{el} < 0$ , there is no more energy barrier (see fig.2 right). In both regimes, the two poles on the sphere Donor and Acceptor are surrounded by periodic and stable orbits with frequency  $\omega_{el}$  obtained by linearizing the equations (3) which turns out to be related to  $|E_{el}| = \hbar\omega_{el}$ . When this electronic frequency  $\omega_{el}$  is beyond the phonon spectrum that is  $\omega_{el} \gg \omega_c$ , the damping terms have no dissipative effect in eqs.3 so that the poles are really stable at 0K. Then, the thermal random forces in eq.3 are necessary to bring the electronic levels near resonance where the damping terms

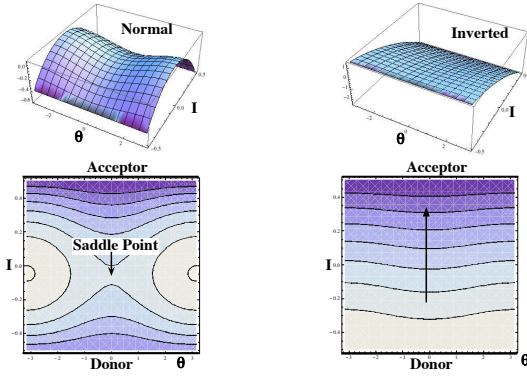


FIG. 2: Some 3D plot and below their corresponding contour plots for the energy landscape  $H_{eff}(I, \theta)$  on the sphere  $I, \theta$  (represented with the Mercator projection where the poles are single points appearing as the thick lines) in cases with no covalent interactions ( $\Gamma_{xx}(0) = \Gamma_{xz}(0) = 0$  and  $\Gamma_{zz}(0) = 1$ ). On the left side :  $\epsilon_z = 0.1$ ,  $\epsilon_x = -0.1$  corresponds to a normal regime in the standard theory (see fig.1) and on the right side  $\epsilon_z = 1$ ,  $\epsilon_x = -0.1$  to an inverted regime.

become efficient in eqs.3. We have already shown in [7] that reaching this resonance is equivalent to reach the intersection between the two paraboloids so that we recover an Arrhenius law. On contrary, in the inverted regime but near the inversion point where  $\omega_{el} < \omega_c$ , ET spontaneously occurs at 0K (and very fast) since the phonon bath can absorb efficiently the reaction energy.

When  $\Gamma_{zz}(0) \ll \Gamma_{xx}(0)$  and  $\epsilon_z < \Gamma_{xx}(0)$  (then  $\Gamma_{xx}(0) \gg |\Gamma_{xz}(0)|$ ), there are two energy minima on the sphere (see fig.3 left) corresponding both to covalent bonds where  $\theta = 0 \bmod \pi$  and  $I = I_c \approx \frac{\epsilon_z}{2\Gamma_{xx}(0)}$  with  $|I_c| < 1/2$  and two maxima on  $\theta = \pi/2 \bmod \pi$ . Actually, only the lowest minimum is physically acceptable for the covalent bond [9]. The poles  $I = \pm 1/2$  are unstable because they belong to large amplitude time periodic orbits with a low frequency in the range of phonon frequencies. These trajectories are dissipative and start to converge toward the minimum energy solution which is the covalent bond. This is the situation of free radicals which spontaneously bind without activation energy.

The most interesting situation is obtained in the intermediate case, when both charge and covalent interactions are present. Fig.3 shows the ideal case obtained for well chosen parameters where  $\epsilon_x = \epsilon_z = 0$ ,  $\Gamma_{xx}(0) = \Gamma_{zz}(0)$ ,  $\Gamma_{xz}(0)$ . Then  $H_{eff}(I, \theta)$  is minimum along two degenerate paths  $\theta = 0$  or  $\pi/2$  which is quite similar to those of a dimer model with Targeted Energy Transfer [5]. Again because of [9], only one of these paths physically exist. Actually for model parameters near but not equal to their ideal values, the energy profile between Donor and Acceptor is rather flat with small reaction energy for ET positive or negative. When the reaction energy is positive without energy barrier ET occurs spontaneously and

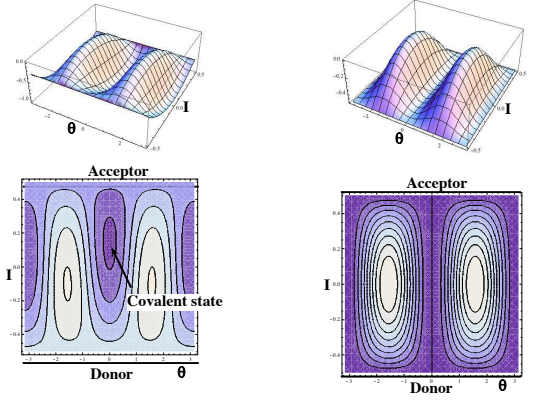


FIG. 3: Same as fig.2 but for some examples with covalent interactions. On the left side  $\epsilon_z = 0.2$ ,  $\epsilon_x = -0.01$ ,  $\Gamma_{zz}(0) = 1$ ,  $\Gamma_{xx}(0) = 2$ , and  $\Gamma_{xz}(0) = -0.1$ . correspond to a situation where the final state is a covalent state. On the right side :  $\epsilon_z = \epsilon_x = 0$ ,  $\Gamma_{xx}(0) = \Gamma_{zz}(0) = 1$ , and  $\Gamma_{xz}(0) = 0$  correspond to an ideally isoenergetic and barrierless situation.

very fast at 0K because the phonon bath is dissipative. ET may be reversed when the reaction energy is negative. If there is a small energy barrier, ET is nevertheless ultrafast but requires a small temperature.

In summary, we have shown that using the complex electronic amplitudes as reaction coordinates (instead of the nuclei coordinates) allows one to treat both charge and covalent interactions. In the limit where only charge interactions are present, we recover the standard redox theory of ET (apart the Landau-Zeener effect concerning the prefactor of the Arrhenius law). With only the covalent interactions, we can model the covalent binding of free radicals. The most interesting result is the possible existence in the intermediate regime of almost barrierless and isoenergetic chemical paths for a two state (or dimer) model as needed for understanding biochemistry.

In further publications, we shall extend this formalism to three states models and in particular reconstruct a physically correct model for ultrafast electron transfer reproducing the same features as in [6, 7]. Variations/extensions of this trimer model will be proposed for ultrafast charge transport (or excitonic) in conducting polymers or along selected paths in proteins, for highly energetic reactions with excitonic storage of the reaction energy, for biomotors (where motion is obtained through molecular reorganisation) etc...

Our enzymatic models require fine tuning of their parameters so that their function can be either blocked, activated or even reversed by changes of the environment involving the solvent (pH, ions concentration) the binding/unbinding of cofactors, changes of conformation etc... then allowing regulation and logics. We believe that complex enzymes involve transitions within a large set of electronic states organized in such a way they operate as logical processing units.

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  - [2] [http://en.wikipedia.org/wiki/Radical\\_\(chemistry\)](http://en.wikipedia.org/wiki/Radical_(chemistry))
  - [3] The assumption that the wave functions defining the base of the invariant subspace  $\psi_D(\mathbf{r}, \mathbf{R})$  and  $\psi_A(\mathbf{r}, \mathbf{R})$  and their overlaps are smoothly dependant on  $\mathbf{R}$ , may be reasonably assumed for the LCAO base but not for other bases such as those of electronic eigenstates.
  - [4] If  $\Psi(0)$  is the wave function at time 0 and  $A(t) = e^{\frac{i}{\hbar}\tilde{H}t} A e^{-\frac{i}{\hbar}\tilde{H}t}$ , the observable of operator  $A$  at time  $t$  is  $\bar{A}(t) = \langle \Psi(0) | A(t) | \Psi(0) \rangle$ . Then  $i\hbar\dot{\bar{A}}(t) = [\tilde{H}, \bar{A}]$ .
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  - [8] We may also assume only few damped modes thermalized by white random forces instead of a phonon continuum. Such an assumption may be convenient for applications.
  - [9]  $\Lambda(\mathbf{R})$  should have a constant sign and exponentially vanish at large distance Donor-Acceptor. However, because of the linear approximation on  $\Lambda(\mathbf{R})$  in (1), it may change sign instead of vanishing. Thus potential  $H_{eff}(I, \theta)$  is well-described only on the part of the sphere where  $\Lambda(\mathbf{R})$  keep the same sign as  $\Lambda(\mathbf{0})$ . Thus, one of its two minima is an artefact which does not correspond physically to a covalent bond.